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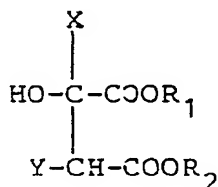
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(54) Surfactants coming from bi- or tri-carboxylic hydroxyacids.

(57) There are disclosed surfactants consisting of esters of bi-or tri-carboxylic hydroxyacids having general formula:



wherein:

X = H, -CH₂COOR;

Y = H, OH, on condition that Y = H when X = -CH₂COOR;

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R, R₁, R₂, which may be the same or different, are H, an alkaline or alkaline-earth metal, -NH₄, a cation of an ammonium organic base or an A radical selected from the group comprising etherified (C₆-C₁₆) alkyl polysaccharides containing from 2 to 6 saccharide units and etherified (C₆-C₁₆)hydroxyalkyl aliphatic polyalcohols containing from 2 to 16 hydroxyl groups and wherein at least one of said R, R₁, R₂ is an A radical.

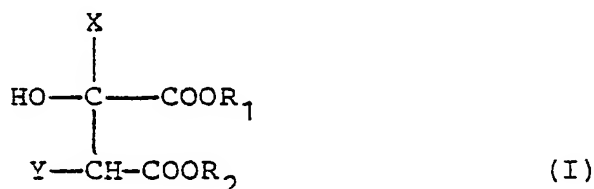
SURFACTANTS COMING FROM BI-OR TRI-CARBOXYLIC HYDROXYACIDS

The present invention relates to surfactants coming from bi-or tri-carboxylic hydroxyacids with polyhydroxylated compounds.

In the great deal of classes of known surfactants it is difficult to find a group of characteristics being all joint in an only product, such as biodegradability, untotoxicity, lack of irritant effects on the skin, a high water solubility in addition to excellent detergent properties, that make such a product particularly versatile and therefore make it utilisable equally for the most different uses such as, for instance, detergency in general, toilette field, beauty culture, foodstuff industry, textile industry, emulsion polymerization and so on.

We have now found surfactants coming from bi-or tri-carboxylic hydroxyacids, more particularly consisting of esters of citric, tartaric or malic acid with alkyl ethers of polysaccharides or with hydroxyalkylethers of polyalcohols, as well as of salts thereof with inorganic or organic bases, which surfactants have, in combination, aforesaid good characteristics and therefore proved to be suitable for a great deal of applications.

Therefore the object of the present invention concerns the esters of bi-or tri-carboxylic hydroxyacids having general formula:



wherein:

X is H or $-\text{CH}_2\text{COOR}$ group;

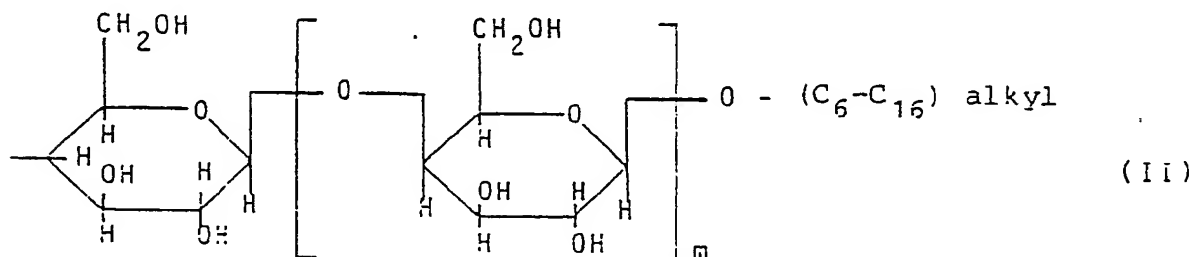
Y is H or $-\text{OH}$, on condition that Y is H when X is $-\text{CH}_2\text{COOR}$;

R, R₁, R₂, which may be the same or different, represent a hydrogen atom, an alkaline or alkaline-earth metal, an ammonium group, the cation of an ammonium organic base or an A radical coming from a polyhydroxylated organic compound selected from the group comprising etherified (C₆-C₁₆) alkyl polysaccharides containing from 2 to 6 monomeric saccharide units and etherified (C₆-C₁₆) hydroxyalkyl aliphatic polyalcohols containing from 2 to 16 hydroxyl radicals, on condition that at least one of said R, R₁, R₂ is an A radical and wherein hydroxyl radical or hydroxyl radicals of the acid group of the ethers having formula (I) may be optionally esterified or etherified by usual methods.

The alkaline metal is selected preferably between sodium and potassium and the alkaline earth metal is preferably magnesium.

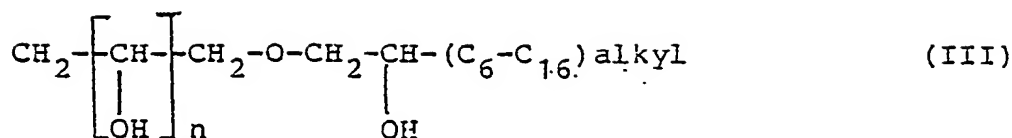
The cation of an ammonium organic base may come, for instance, from an alkanolamine such as monoethanolamine or triethanolamine.

As A radicals coming from etherified (C₆-C₁₆) alkyl polysaccharides, use may be made, for instance, of the ones coming from monoalkyletherified polyglucose having formula:

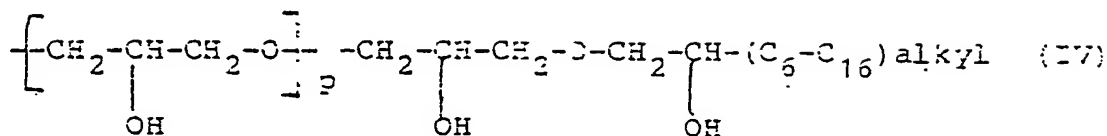


wherein m is a whole number ranging from 1 to 5.

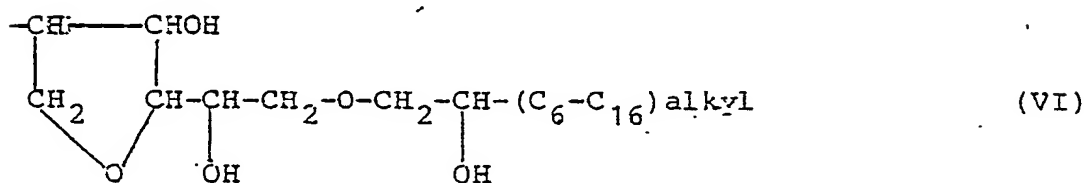
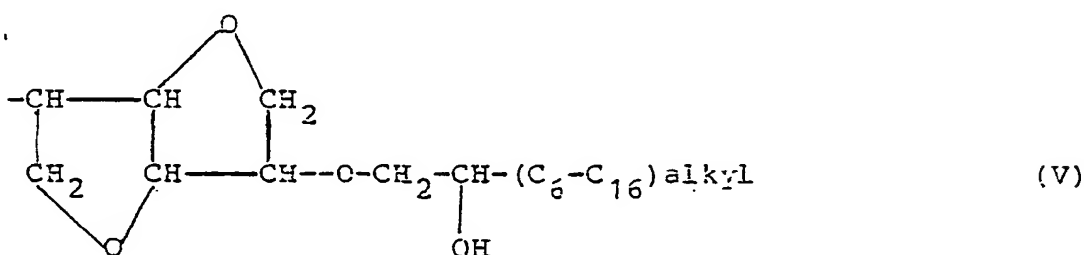
As A radicals, coming from etherified (C₆-C₁₆) hydroxyalkyl aliphatic polyalcohols, use may be made, for instance, of the ones having general formulae:



wherein n is a whole number ranging from 1 to 15;



wherein p is a whole number ranging from 1 to 10;

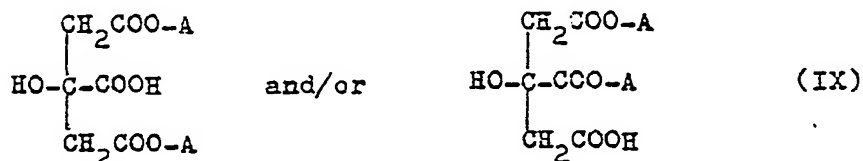
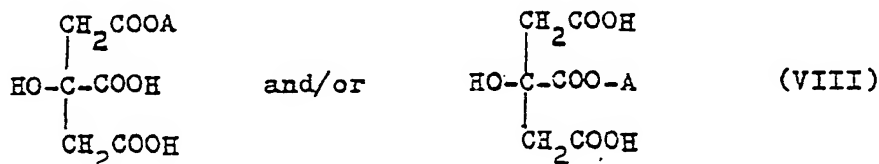


The esters having formula (I) are prepared according to a process, and this forms a further object of the present invention, comprising esterification of citric, tartaric or malic acid with a polyhydroxylated organic compound having formula:

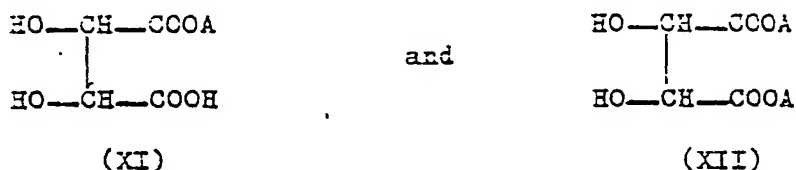
A-OH (VII)

wherein A has aforesaid meaning, by heating at a temperature of 120-140°C, with continuous distillation of the water forming during the reaction and optional final salification of the obtained product by means of bases of alkaline or alkaline-earth metals, ammonia or amines. As base use may be made, for instance, of sodium, potassium, magnesium, ammonium hydroxide, triethanolamine or monoethanolamine.

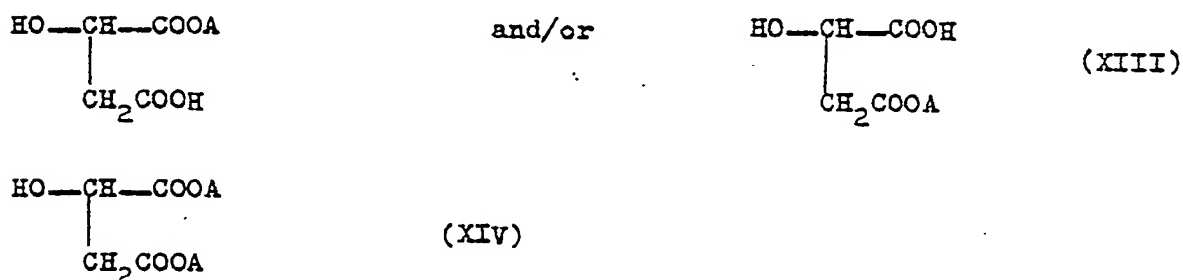
By aforesaid process, starting from citric acid, one obtains mono-di-and triesters having the following formulae respectively:



Starting from tartaric acid one obtains mono-, and di-esters having the following formulae respectively:



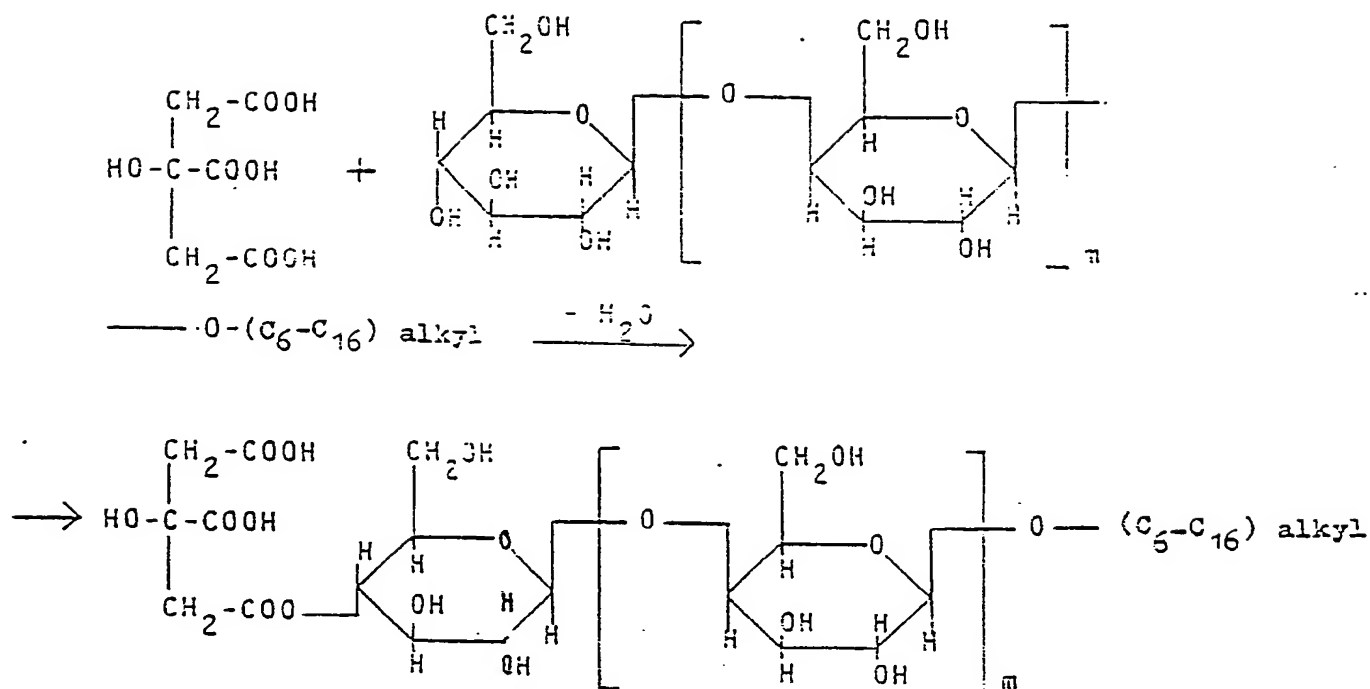
Starting from malic acid one obtains mono- and di-esters having the following formulae respectively:



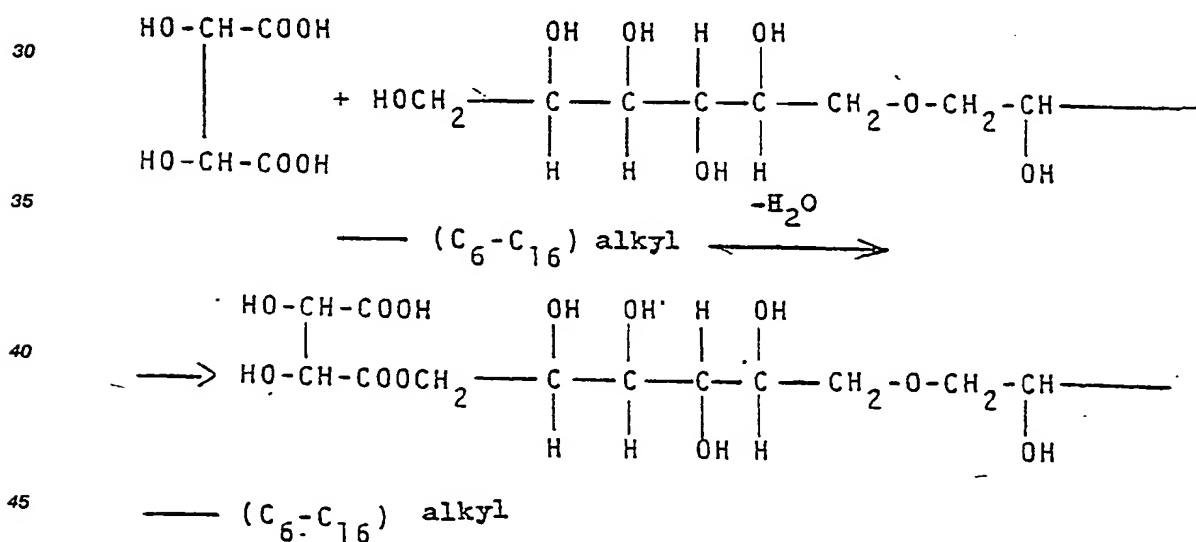
According to the employed reaction conditions and according to the molar ratios hydroxyacid/polyhydroxylated compound it is possible to prepare in preference mono-, di- and in the case of citric acid, tri-ester as well.

Thus hydroxyacid and polyhydroxylated compound (VII) are reacted in substantially equimolecular ratios in order to produce preferably monoesters having formulae (VIII), (XI) and (XIII).

In the case of the preparation of citric monoester of monoalkyletherified polyglucose, the reaction may be carried out according to the following equation:



In the case of the preparation of tartaric monoester of monohydroxyalkyletherified sorbitol, the reaction may be carried out according to the following equation:



The polyhydroxylated organic compounds having formula (VII), such as alkyletherified polysaccharides and hydroxyalkyletherified polyalcohols are known products or may be prepared by known methods and sometimes they may be found on the market.

In particular the monoalkyletherified polysaccharides may be prepared by etherification of the polysaccharide with (C₅-C₁₆) fatty alcohols.

The monohydroxyalkyletherified polyalcohols may be prepared by reaction of the polyalcohol with a (C₅-C₁₆) alkyl α-epoxide.

Among the alkyletherified polysaccharides preference is given to polyglucose monoalkyletherified with octylic and decylic alcohols.

Among the hydroxyalkyletherified polyalcohols preference is given to sorbitol monohydroxyalkyletherified with octene-1-oxide and/or decene-1-oxide.

The esters according to the present invention and in particular the monoesters of alkyletherified polysaccharides or of hydroxyalkyletherified polyalcohols, salts and mixtures thereof are very efficient surfactants, allowing, even when employed in very low percentages, a remarkable lowering of the surface tension and therefore they may be used as emulsifiers, dispersing agents or detergents in general.

Besides the excellent detergent properties, they do not present any toxic effect, as well as any irritant effect on skin and eyes and they do not present any acute toxicity if they are swallowed orally.

They are highly biodegradable, showing biodegradability values over 90%.

They prove to be stable within a wide range of temperatures up to 100°C and after a storage at low temperatures for a long time, when they are brought to room temperature, do not give rise to any separation.

They show a good but not excessive wetting power and a good foam forming power. They may have from a moderate to an excellent water solubility.

In particular their solubility increases, by increasing the number of hydroxyl radicals of the polyhydroxylic part of the alkyletherified or hydroxyalkyletherified compound.

The esters, according to the invention, proved to be compatible with most of known surfactants and therefore they may be formularized with them.

The esters, according to the invention, on account of their whole of characteristics, proved to be very flexible as to the different applications of the surface-active agents.

On account of their high detergent power joint to lack of toxic effects on the skin, hair, eyes, the esters are particularly suitable for their applications in the beauty culture field such as, for instance, for the preparation of liquid or creamy detergents for the skin, shampoos, bath foams.

The following examples will illustrate the invention, without limiting, however, its scope.

EXAMPLE 1

Preparation of esters of citric acid by polyglucose monoalkylethers.

Esterification

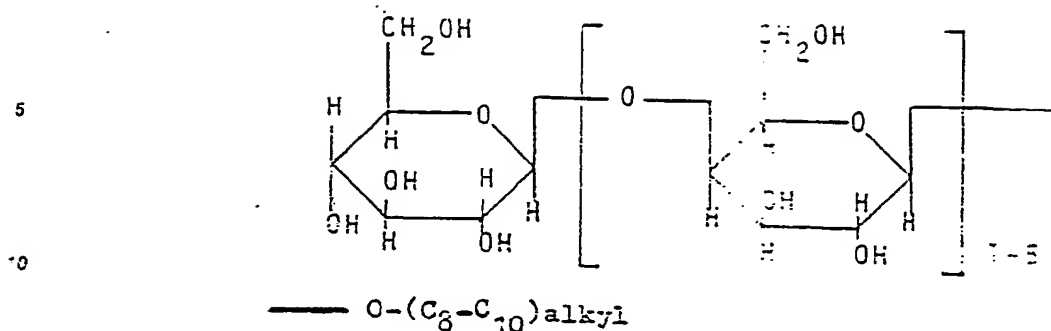
144.0 g (0.75 moles) of anhydrous citric acid and 784.9 g (0.75 moles) of TRITON-CG/110® at 60% in water were fed, under nitrogen flow, into a reactor equipped with a heating system, stirrer, vacuum pipe connection, thermometer, system for feeding the reactants and connected to a cooler equipped with a manifold for collecting the dilution water and successively the reaction water.

Vacuum was produced inside the apparatus, by means of a water pump, and while keeping the mixture under stirring, the temperature was brought to 90°-105°C, in about 40 minutes in order to remove the dilution water, afterwards, vacuum was stopped and the temperature was brought to 124-125°C under nitrogen flow; the reaction mixture was kept at this temperature over about 100 minutes, till acid value was 145± 3.

The mixture was cooled up to a temperature of 110°-115°C, diluted with about 300 g of water, equal to 50% of the calculated amount of acid monoester, cooled up to 50°C and finally the reactor was unloaded.

One obtained 900 g of a limpid liquid product containing 33.33% of water, having an acid value of 97.4 and a saponification number of 140, substantially consisting of citric acid monoester.

TRITON-CG/110® consisted of a mixture of polyglucose monoalkylethers at 60% in water of formula:



15 having a hydroxyl number of 879.9, determined on the dry product, obtained by etherification of poly-glucose containing from 2 to 6 glucose units with a mixture 50/50 of octylic and decylic alcohol.

Salification

20 339.6 g of the citric monoester at 66.66% in water, prepared before and 581.7 g of demineralized water were fed into a vessel equipped with a stirrer, thermometer, dropping funnel and water cooling system.

The mixture was stirred till a limpid solution was obtained, afterwards, under stirring, 78.7 g of an aqueous solution of NaOH at 30% were fed slowly, in about 1 hour, through a dropping funnel, while keeping the temperature at values below 30°C.

25 One obtained 1000 g of a limpid aqueous solution containing 25% by weight of citric monoester salified with sodium.

The solution, thus obtained, could be employed, either as such or after having been diluted, for the different uses of detergency.

30 An utter viscous limpid liquid was obtained from the solution, after having removed the water by heating at 50°C over 16 hours under vacuum; such a liquid consisted prevalingly of sodic salt of citric monoester, having an acid value of 5, a saponification number of 71.0, an esterification number of 66.0 and a pH value of 6.8 at 1%.

The salified product proved to be perfectly soluble in water in any ratio, yielding limpid solutions at 25°C up to a concentration of 25% and more or less viscous solutions at higher concentrations.

35 Moreover the following tests were carried out on the salified product:

-Surface tension

40 The surface tension, measured at 20°C according to DU NOUY method, was 42.0 dynes/cm at a concentration of 0.25 g/l and 32.3 dynes/cm at a concentration of 1 g/l.

-Imbibition power

45 Imbibition power, determined on the product at a concentration of 2 g/l in distilled water, was over 1800 seconds.

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-Foam forming power

It was determined on 200 ml of an aqueous solution containing 2 g/l of the product, by using a bored flat piston system, 50 strokes. The following results were obtained:

	After minutes	foam ml
5	0	790
10	5	780
	10	770
15	15	770
	20	770
20	25	760
	30	760

Moreover the salified product proved to be highly biodegradable, unotoxic, unimutagenic and endowed with an excellent detergent power.

30 EXAMPLE 2

Preparation of esters of tartaric acid by polyglucose monoalkylethers.

35 Esterification

75.1 g (0.5 moles) of anhydrous tartaric acid and 523.2 g (0.5 moles) of TRITON-CG/110® at 60% in water were fed, under nitrogen flow, into a reactor equipped with a heating system, stirrer, vacuum pipe connection, thermometer, system for feeding the reactants and connected to a cooler equipped with a manifold for collecting the dilution water and successively the reaction water.

Vacuum was produced inside the apparatus, by means of a water pump, and while keeping the mixture under stirring, the temperature was brought to 90-105°C in about 50 minutes, in order to remove the dilution water, afterwards, vacuum was stopped and the temperature was brought to 118-120°C under nitrogen flow; the reaction mixture was kept at this temperature over about 90 minutes, till acid value was 85± 3.

The mixture was cooled up to a temperature of 110-115°C, diluted with about 188 g of water, equal to 50% of the calculated amount of acid monoester, cooled up to about 50°C and finally the reactor was unloaded.

One obtained 564 g of a limpid liquid product, containing 33.33% of water, having an acid value of 50.0 and a saponification number of 98.4, substantially consisting of tartaric acid monoester.

Salification

356.1 g of the tartaric monoester at 66.66% in water, prepared before, and 601.5 g of demineralized water were fed into a vessel equipped with a stirrer, thermometer, dropping funnel and water cooling system.

The mixture was stirred till a limpid solution was obtained. afterwards, under stirring 42.4 g of an aqueous solution of NaOH at 30% were fed, slowly in about 1 hour, through a dropping funnel, while keeping the temperature at values below 30°C.

One obtained 1000 g of a limpid aqueous solution containing 25% by weight of tartaric monoester, salified with sodium.

The solution, thus obtained, could be employed, either as such or after having been diluted, for the different uses of detergency.

An utter viscous limpid liquid was obtained from the solution, after having removed the water by heating at 50°C over 16 hours, under vacuum; such a liquid consisted prevailingly of sodic salt of tartaric monoester, having an acid value of 2.4, a saponification number of 77.2, an esterification number of 74.8 and a pH value of 6.8 at 1%.

The salified product proved to be perfectly soluble in water in any ratio, yielding limpid solutions at 25°C up to a concentration of 25% and more or less viscous solutions at higher concentrations.

Moreover the following tests were carried out on the salified product:

-Surface tension

The surface tension, measured at 20°C, according to DU NOUY method, was 43.5 dynes/cm at a concentration of 0.25 g/l and 30.0 dynes/cm at a concentration of 1 g/l.

-Imbibition power

Imbibition power, determined on the product at a concentration of 2 g/l in distilled water, was over 1800 seconds.

-Foam forming power

It was determined on 200 ml of an aqueous solution containing 2 g of the product, by using a bored flat piston system, 50 strokes. The following results were obtained:

	After minutes	foam ml
35	0	790
	5	780
40	10	780
	15	780
45	20	770
	25	770
50	30	760

Moreover the salified product proved to be highly biodegradable, un toxic, un irritant and endowed with an excellent detergent power.

EXAMPLE 3

Preparation of monoester of citric acid by sorbitol 2-hydroxyoctyl-ether.

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Esterification

126.7 g (0.66 moles) of anhydrous citric acid and 200.0 g (0.66 moles) of sorbitol 2-hydroxyoctyl-ether were fed, under nitrogen flow, into a reactor equipped with a heating system, stirrer, thermometer, system for feeding the reactants and connected to a cooler equipped with a manifold for collecting the reaction water.

The temperature was brought, under stirring and nitrogen flow, to 140-142°C in about 90 minutes and the reaction mixture was kept at this temperature for about 50 minutes, till acid value was 240± 5.

The mixture was cooled up to a temperature of 110-115°C, diluted with about 157 g of water, equal to 50% of the calculated amount of acid monoester, cooled up to 50°C and finally the reactor was unloaded.

One obtained 471 g of a viscous liquid containing 33.33% of water, having an acid value of 156.8 and a saponification number of 235.2, substantially consisting of citric acid monoester.

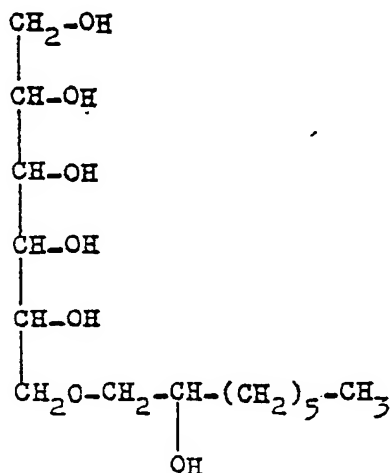
Sorbitol 2-hydroxyoctyl-ether having formula:

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having a hydroxyl number of 1111.0 and a molar weight of 303, was obtained, by reacting sorbitol with octene-1-oxide.

40

Salification

321.2 g of the citric monoester at 66.66% in water, prepared before, and 559.2 g of demineralized water were fed into a vessel equipped with a stirrer, thermometer, dropping funnel and water cooling system.

The mixture was stirred till a homogeneous emulsion was obtained, afterwards under stirring, 119.6 g of an aqueous solution of NaOH at 30% were fed slowly in about 1 hour, through a dropping funnel, while keeping the temperature at values below 30°C.

1000 g of a slightly cloudy aqueous solution were obtained. Then by paper filtration one obtained a limpid aqueous solution containing 25% by weight of citric monoester salified with sodium.

The solution, thus obtained, may be used either as such or after having been diluted, for the different uses of detergency.

An utter viscous limpid liquid was obtained from the solution, after having removed the water by heating at 50°C over 16 hours under vacuum; such a liquid consisted prevalingly of sodic salt of citric monoester, having an acid value of 4.5, a saponification number of 119.4, an esterification number of 114.9 and a pH value of 6.8 at 1%.

The salified product proved to be perfectly soluble in water in any ratio, yielding limpid solutions at 25°C up to a concentration of 25% and more or less viscous solutions at higher concentrations.

The following tests were carried out on the salified product:

-Surface tension

The surface tension, measured at 20°C, according to DU NOUY method, was 29.5 dynes/cm at a concentration of 0.25 g/l and 27.5 dynes/cm at a concentration of 1 g/l.

-Imbibition power

Imbibition power, determined on the product at a concentration of 2 g/l in distilled water was over 1800 seconds.

-Foam forming power

It was determined on 200 ml of an aqueous solution, containing 2 g/l of the product, by using a bored flat piston system, 50 strokes. The following results were obtained:

	After minutes	foam ml
	0	530
	5	530
	10	520
	15	510
	20	480
	25	450
	30	410

Moreover the salified product proved to be highly biodegradable, un toxic, un irritant and endowed with an excellent detergent power.

Claims

1. Esters of bi-or tri-carboxylic hydroxyacids having general formula:



wherein:

X is H or -CH₂COOR group;

Y is H or -OH, on condition that Y is H when X is -CH₂COOR;

R, R₁, R₂, which may be the same or different, represent a hydrogen atom, an alkaline or alkaline-earth metal, an ammonium group, the cation of an ammonium organic base or an A radical coming from a polyhydroxylated organic compound selected from the group comprising etherified (C₆-C₁₆) alkyl polysaccharides containing from 2 to 6 monomeric saccharide units and etherified (C₆-C₁₆) hydroxyalkyl aliphatic polyalcohols containing from 2 to 16 hydroxyl radicals, on condition that, at least one of said R, R₁, R₂, is an A radical.

2. Esters, according to claim 1, wherein A radical is selected from the group comprising polyglucose (C₆-C₁₆) monoalkyl ethers, containing from 2 to 6 glucose units and sorbitol (C₆-C₁₆) monohydroxyalkyl ethers.

3. Esters according to one or both of the claims 1-2, wherein the hydroxyl radical or the hydroxyl radicals of the acid group of the esters having formula (I) are esterified or etherified by usual methods.

4. Esters according to claim 1, namely citric acid monoesters, with polyglucose (C₆-C₁₀) monoalkylethers containing from 2 to 6 glucose units and salts thereof with inorganic or organic bases, respectively, or with sorbitol 2-hydroxyoctylether and salts thereof with inorganic or organic bases, respectively.

5. Esters according to claim 1, namely tartaric acid monoesters, with polyglucose (C₆-C₁₀) monoalkyl ethers, containing from 2 to 6 glucose units and salts thereof with inorganic or organic bases, respectively, or with sorbitol 2-hydroxy octylether and salts thereof with inorganic or organic bases, respectively.

6. A process for preparing the esters having formula (I) according to claim 1, consisting in esterifying citric, tartaric or malic acid with a polyhydroxylated compound having formula:

A-OH (VIII)

wherein A has the meaning according to claim 1, by heating at a temperature of 120-140°C, with continuous distillation of the water forming during the reaction and optional salification of the obtained product, with bases of alkaline or alkaline-earth metals, ammonia or amines.

7. A process according to claim 6, wherein A radical is selected from the group comprising polyglucose (C₆-C₁₆) monoalkyl ethers containing from 2 to 6 glucose units and sorbitol (C₆-C₁₆) monohydroxyalkyl ethers.

8. Cosmetic and detergent compositions containing one or more esters according to one or more of the claims form 1 to 5.

9. Use of the esters according to one or more of the claims 1-5, as surface-active agents.





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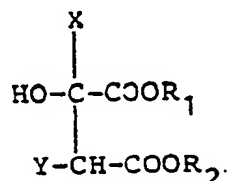
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(54) Surfactants coming from bi- or tri-carboxylic hydroxyacids.

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wherein:

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Y = H, OH, on condition that Y=H when X = -CH₂COOR;

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EP 0 258 814 A3



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

EP 87 11 2430

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
A	DE-A-2 148 279 (UNILEVER) * Claims 1-13 * ---	1,8,9	C 07 H 15/04 C 07 C 69/708
A	DE-A-2 304 057 (UNILEVER) * Claims 1-14 * ---	1,8,9	C 11 D 1/08 A 61 K 7/08 A 61 K 7/50
A	US-A-3 661 955 (A.P. CENTOLELLA et al.) * Column 1, lines 12-51; claim 1 * ---	1,8,9	
A	FR-A-2 153 448 (KNAPSACK) * Claims 1-8 * ---	1,8,9	
A	FR-A-2 153 449 (KNAPSACK) * Claims 1-7 * -----	1,8,9	
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)
			C 07 H 15/00 C 07 C 69/00
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 19-04-1990	Examiner BRENNAN J.
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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